

FINAL

Technical Support for West Virginia Ionic Toxicity TMDLs Model Selection

January 17, 2020
Version 2.0

PRESENTED TO

**United States EPA Region 3
West Virginia DEP**

PREPARED BY

Tetra Tech
10306 Eaton Place, Suite 340
Fairfax, VA 22030

TABLE OF CONTENTS

1.0 IONIC TOXICITY INTRODUCTION AND MODELING REQUIREMENTS.....1

2.0 PREVIOUS WORK AND AVAILABLE MODELING TOOLS5

3.0 MDAS INTRODUCTION AND PREVIOUS WORK6

4.0 SUMMARY 13

5.0 REFERENCES 13

1.0 IONIC TOXICITY INTRODUCTION AND MODELING REQUIREMENTS

All West Virginia waters are subject to the narrative criteria in Section 3 of the Requirements Governing Water Quality Standards (Title 47 CSR Series 2). That section, titled “Conditions Not Allowable in State Waters,” contains various general provisions related to water quality. The narrative water quality criterion at Title 47 CSR Series 2 – 3.2.i prohibits the presence of wastes in state waters that cause or contribute to significant adverse impacts to the chemical, physical, hydrologic, and biological components of aquatic ecosystems. Assessment of the biological integrity of a stream is based on a survey of the stream’s benthic macroinvertebrate community. Biological assessments are useful in detecting impairment, but they may not clearly identify the causes of impairment, which must be determined before TMDL development can proceed. USEPA developed *Stressor Identification: Technical Guidance Document* (Cormier et al., 2001) to assist water resource managers in identifying stressors and stressor combinations that cause biological impairment. Elements of the SI process are used to evaluate and identify the significant stressors to the impaired benthic communities. In addition, custom analyses of biological data are performed to supplement the framework recommended by the guidance document.

TMDL development in biologically impaired waters requires identification of the pollutants that cause the stress to the biological community. The candidate causes responsible for biological impairments are listed below and conceptualized in Figure 1:

1. Metals contamination (including metals contributed through soil erosion) causes toxicity
2. Acidity (low pH) causes toxicity
3. Basic (high pH >9) causes toxicity
4. Increased ionic strength causes toxicity
5. Organic enrichment (e.g. sewage discharges and agricultural runoff cause habitat alterations)
6. Increased metals flocculation and deposition causes habitat alterations (e.g., embeddedness and cementation of substrate)
7. Increased total suspended solids (TSS)/erosion and altered hydrology cause sedimentation and other habitat alterations
8. Altered hydrology causes higher water temperature, resulting in direct impacts to survivability and community composition
9. Altered hydrology, nutrient enrichment, and increased biochemical oxygen demand (BOD) cause reduced dissolved oxygen (DO)
10. Algal growth causes food supply shift
11. High levels of ammonia cause toxicity (including increased toxicity due to algal growth)
12. Chemical spills cause toxicity

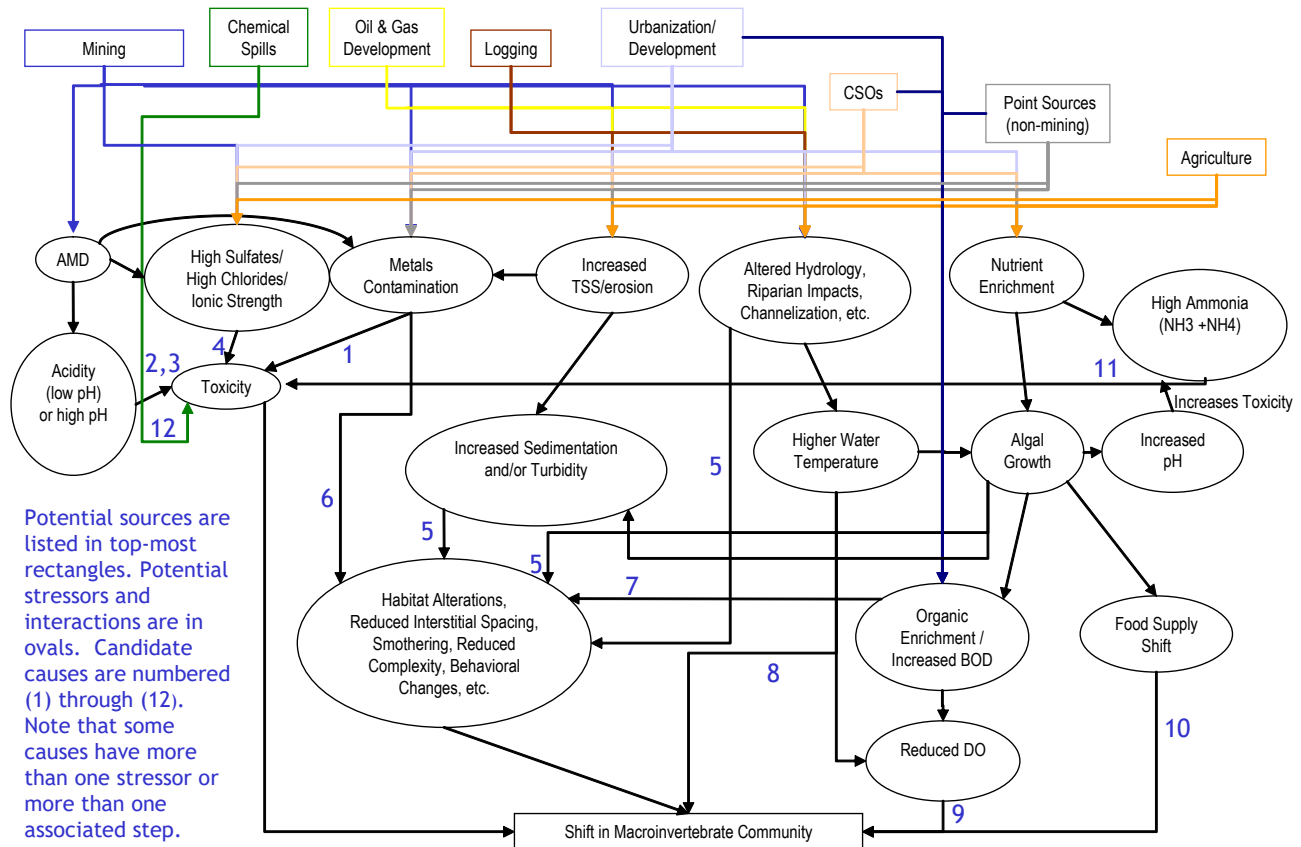


Figure 1. Conceptual model of candidate causes and potential biological effects.

Streams in which ionic toxicity is identified as a significant stressor typically have a strong presence of dissolved ions such as sulfates, bicarbonate, chloride, and elevated conductivity. Other dissolved ions such as sodium, calcium, potassium, and magnesium are required to be analyzed as well. Potential sources of both natural and anthropogenic ionic inputs include: active and legacy mining activities, urban stormwater, oil and gas operation, industrial wastewater discharge, road salts, agricultural management, and atmospheric deposition. The model selected for ionic toxicity assessment should be able to simulate geochemical speciation of dissolved ions and represent the mentioned potential sources and pathways in the model.

Geology contributes to the natural ionic condition of waterbodies. Limestone/dolomite (karst landforms); marine mudstones and shales; siliceous sandstones and quartzite all help define regional and subregional boundaries and have different ionic characteristics. West Virginia's land includes portions of 4 Level III Ecoregions, and many more Level IV subregions. The Lower Guyandotte River Watershed (Figure 2) is in Ecoregions 69d and 70b. Differences among ecoregions are attributable to elevation, landform, underlying geology, natural vegetation and land use. Geology contributes to the natural ionic condition of waterbodies: limestone/dolomite (karst landforms); marine mudstones and shales; siliceous sandstones and quartzite all help define regional and subregional boundaries. Furthermore, geologic conditions in ecoregions 69 and 70 exhibit higher sulfate concentrations than other regions of WV. Although the affected streams for the pilot project may be of similar geochemical composition and have similar ion sources, the selected model needs to be capable of simulating specific ions associated with ionic toxicity under various geochemical baselines.

To address these specific complexities in hydrological and geochemical processes in West Virginia, the selected model needs to:

- Simulate hydrologic variations due to time variable weather patterns and the related transient saturation or unsaturated condition of the surface/subsurface;
- Represent varied potential loading sources and simulate time variable chemical loadings from varied sources;
- Simulate dynamic geochemical interactions within a stream channel with specific speciation;
- Simulate components in all three phases: dissolved, solids, and adsorbed with multiple chemical species, including pH calculation based on thermodynamics and chemical kinetics;
- Include both an equilibrium calculation for the major reactions in stream segments and for certain kinetics-limited reactions, such as the oxidation of ferrous iron to ferric iron or the adsorption of metals on iron oxyhydroxides;
- Provide model results for a broad range of spatial and temporal scales;
- Evaluate source loading abatement scenarios for water quality control/management design, to attain realistic stream chemical conditions and to support various stream conditions affected by anthropogenic or natural sources.

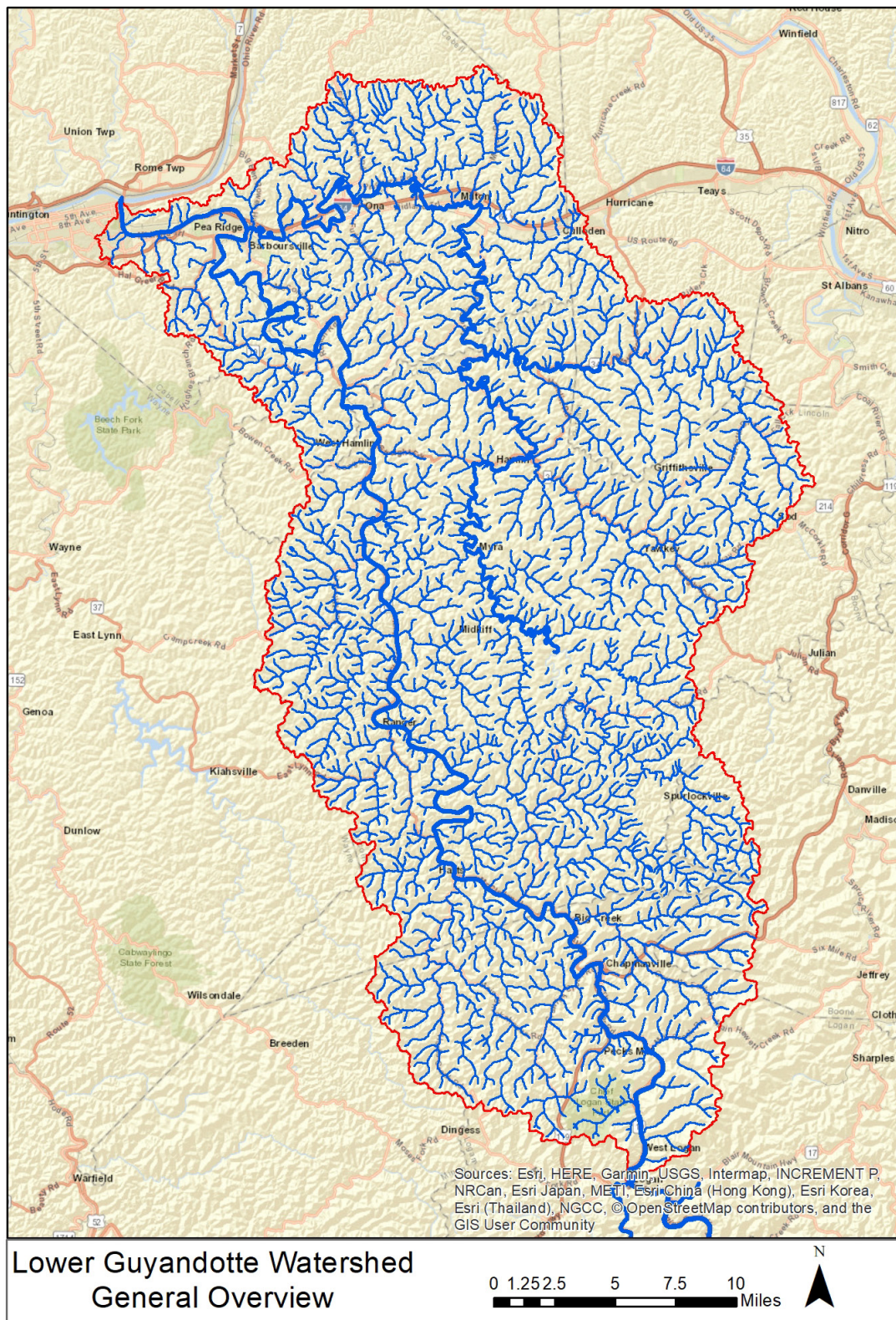


Figure 2. Lower Guyandotte River watershed.

2.0 PREVIOUS WORK AND AVAILABLE MODELING TOOLS

Elevated dissolved material has been identified as a stressor to the aquatic life in Central Appalachian streams (EPA, 2011). The dissolved material is composed of a large array of chemical constituents. Major cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) and anions (Cl^- , HCO_3^- , CO_3^{2-} , SO_4^{2-}) in streams are the most common contributors to dissolved ions. Other water quality constituents including dissolved iron (Fe^{2+}), dissolved aluminum (Al^{3+}), and dissolved manganese (Mn^{2+}), may also contribute to dissolved ions in acid mine drainage (AMD) dominated streams. In most mountainous streams, nitrogen compounds (NH_4^+ , NO_3^- , NO_2^-) and phosphate (PO_4^{3-}) are minor contributors to dissolved ions because of their relatively low concentrations (Stumm and Morgan, 1996).

Currently the TMDL restoration endpoint(s) for ionic toxicity is under development in West Virginia. Total dissolved solids (TDS) is a measurement of all the ions in water. Specific conductivity is commonly used as a surrogate measure of TDS concentration. Conductivity (the ability of a material to conduct an electric current measured in $\mu\text{S}/\text{cm}$ standardized to 25°C) is an easy to use estimate of the ionic strength. For most surface waters, the values of TDS and conductivity are in good correlation to each other and can be converted using linear regression equations (Chapra, 1997). Nationally, several TMDLs have been developed to address salinity or ionic stress issues. Most of the TDS or conductivity TMDLs were developed using the simple load duration curve approach. For example, specific conductance (SC) TMDLs were developed for selected reaches in the Upper Rio Grande watershed using TDS as a surrogate (NMDE, 2004). The TDS:SC ratios of 0.69 and 0.74 were determined for the Rio Grande del Rancho and Rio Fernando de Taos, respectively, using the water quality sampling data. The TMDLs were calculated using the load duration curve method with 4Q3 critical low flow. The load duration curve method was also used to develop TMDLs for chloride, sulfate, and TDS for Bayou Bartholomew Watershed, Arkansas, where irrigation water was determined as the primary pollutant source (USEPA, 2008).

In streams of West Virginia, drainage from a mixture of current and historical mining activities appears to be a major source of dissolved ions. High concentrations of sulfate (SO_4^{2-}) are normally found in the mine water as a result of the dissolution of sulfide rocks after the minerals are exposed to oxygen and water (VADEQ, 2010). Release of brine water with high concentrations of chloride (Cl^-) from oil and gas drilling wells might also be an important ion source. Other sources, including road salt application, failing septic systems, straight pipes, and publicly owned treatment works (POTWs), need to be considered in watersheds with substantial residential area. In addition, groundwater flow and atmospheric deposition provide variable background concentrations of ions.

Watershed-based numerical models with hydrologic and water quality simulating capability have been used to develop TDS TMDLs in the last few years to address the ionic stress. A phased TDS TMDL was developed by Virginia Department of Environmental Quality (VADEQ) to address the benthic impairments of North Fork and South Fork Pound River (VADEQ, 2010). The TDS was simulated as a single conservative generalized water quality constituent (GQUAL) in the Hydrological Simulation Program – FORTTRAN (HSPF) model developed for the TMDL watershed. A major limitation of this modeling method is that it does not provide insight into the chemical nature of dissolved ions. The established water quality models (HSPF, LSPC, SWAT, WASP) provide effective hydrologic and transport simulation of general water quality constituents (Bicknell, et al., 1996). However, the watershed models are generally inadequate in modeling chemical reactions. Most water quality models have a relatively comprehensive framework for carbon, nitrogen, and phosphorus cycles, but lack the capability of coupling heat transfer processes with geochemistry and gas conversion. The accurate modeling of dissolved ions should include specific ions or chemical species (including but not necessarily limited to: Cl , SO_4 , Na , K , Mg , Ca , dissolved Fe , Al , Mn , TDS, Alkalinity, and Acidity) and calculate the ionic strength based on the equilibrium speciation.

Geochemical equilibrium speciation models such as MINTQA2 provide algorithms and databases for calculating the equilibrium composition of dilute aqueous solutions in natural aqueous systems (Allison, et al., 1991). Several geochemical modeling codes have been developed over the years and used to model various scenarios. These

include: the Geochemist's Workbench (Bethke, 2009), EQ3/6 (Wolery 1992), Mineql (Westall, 1976), Netpath (Plummer, 1991), Aquachem (Calmbach, 1999), and WHAM (Tipping, 1994). All these models suffer from a lack of hydrological sophistication. Geochemical equilibrium-based models are mainly designed for understanding basic issues in aquatic chemistry. The model development efforts are focused on the geochemical transport and reaction in water bodies or in porous media (groundwater), with special interests on mining, geologic disposal of waste, chemical spillage, etc. Some hydrological processes are not considered or simplified in geochemical models, including snow hydrology, erosion process, vegetation canopy impacts, and others.

In order to have a comprehensive representation of hydrological processes and the ability to interpret and predict geochemical reactions of dissolved ions in water bodies, a generic aqueous ionic toxicity model is required for TMDL development. A combination of watershed models and geochemical models can provide the chemical speciation function of major aqueous ions and cumulative chemical components (TDS, conductivity, alkalinity, and acidity) based on dissolved ion loadings from watersheds. A model with the above mentioned modules will be able assess ionic impacts and to fulfill regulatory requirements for future TMDLs. Modeling individual chemical species will provide the flexibility to consider various endpoints, including for individual ions or cumulative parameters.

3.0 MDAS INTRODUCTION AND PREVIOUS WORK

From 2008 through 2011, Tetra Tech supported EPA Region 3 and WVDEP in the development of a pilot TMDL for ionic toxicity for the Upper Kanawha and Monongahela River watersheds in WV. To address these specific complexities in hydrological processes and geochemical processes, the Mining Data Analysis System (MDAS) was developed, updated, and coupled with EPA's Loading Simulation Program in C++ (LSPC) to provide a tool to address complex watershed management issues associated with high dissolved ion concentrations in West Virginia streams. Initial efforts focused on updating the MDAS model capabilities for dynamic simulation of ionic composition of receiving waters and time variable loadings. Detailed geochemical reactions were integrated into the MDAS model using the same computational methods and thermodynamic equilibrium distribution employed in the MINTEQA2 and MINEQL models. The updated MDAS model code was tested using the Upper Kanawha and Monongahela River watersheds.

MDAS provides a dynamic, continuous simulation of hydrology and water quality processes. The simulation occurs at a user-specified time step. For water quality applications, an hourly time step is typically appropriate. This is sufficient to capture the storm event hydrograph and to represent major wash-off and erosion events.

Hydrology in MDAS is identical to HSPF/LSPC (Figure 3). Multiple hydrologic components are contained within MDAS including precipitation, interception, evapotranspiration (ET), overland flow, infiltration, interflow, subsurface storage, groundwater flow, and groundwater loss. Figure 3 provides a graphical representation of these processes (capitalized acronyms are computer code routine names). Rain falls and lands on constructed landscapes, vegetation, and soil. Varying soil types allow the water to infiltrate at different rates (using the Philip infiltration algorithm) or enter shallow interflow pathways, while evaporation and plant matter exert a demand on available water. Water flows overland and through the soil matrix. The land representation in the MDAS model contains three major flow pathways: surface, interflow, and groundwater outflow.

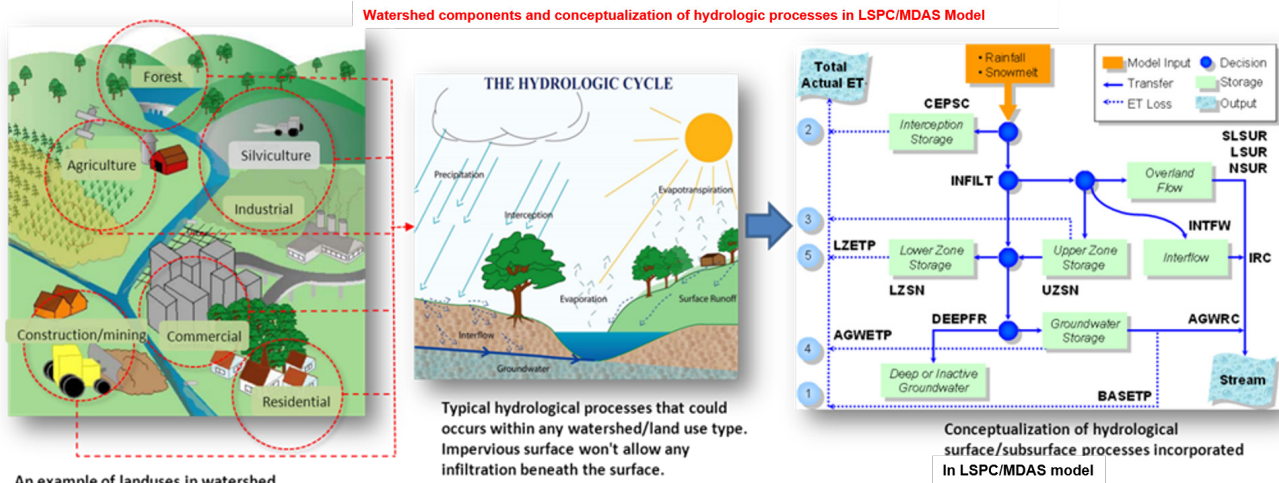


Figure 3. Hydrological component of LSPC model.

The chemical loadings from land are simulated through hydrologic surface and subsurface modeled domains assigned to each land use in the basin. Observed dissolved chemicals (cations and anions) and mineral concentrations with associated observed pH can be assigned to the hydrologic domains/land uses categories of the model initially and then modified during the calibration process. For redox-sensitive chemical pairs, especially iron and manganese in West Virginia's mining-affected streams, the user can apply a defined ratio of the pair (i.e. $\text{Fe}^{2+}/\text{Fe}^{3+}$) in the model. This ratio assignment is due to the fact that certain ions are sensitive to the changes in the redox potential in soils, groundwater, or surface water, which can result in the changes in the ion state of an element. For example, iron in a groundwater environment may be found as ferrous iron (Fe^{2+}) or ferric iron (Fe^{3+}), oxidation states with dramatically different chemical reactivity, transport, and fate, depending on the redox conditions in the groundwater. The assigned chemical concentrations yield time variable chemical/mineral loadings based on simulated time series flows from the hydrologic domains. Input chemical concentrations can be constant throughout the simulation period or vary monthly depending on the available data type and the project objectives. The model also provides two additional functionalities to simulate land surface chemical loadings: 1) chemical build-up/wash-off, and 2) sediment-associated chemicals using potency factors. The land components for MDAS are shown in Figure 4.

The modeled chemical/mineral loadings from the land surface are entered into edge-of-stream calculations to undergo the thermodynamic equilibrium distribution of the assigned chemical components into dissolved chemicals and sediment-associated chemicals. The edge-of-stream calculations use the same computational method employed in MINTEQA2 and MINEQL. The model also provides the option to determine pH, track speciation and adsorption/desorption of the simulated chemicals, and generate land loadings through an additional chemical charge/mass balance method.

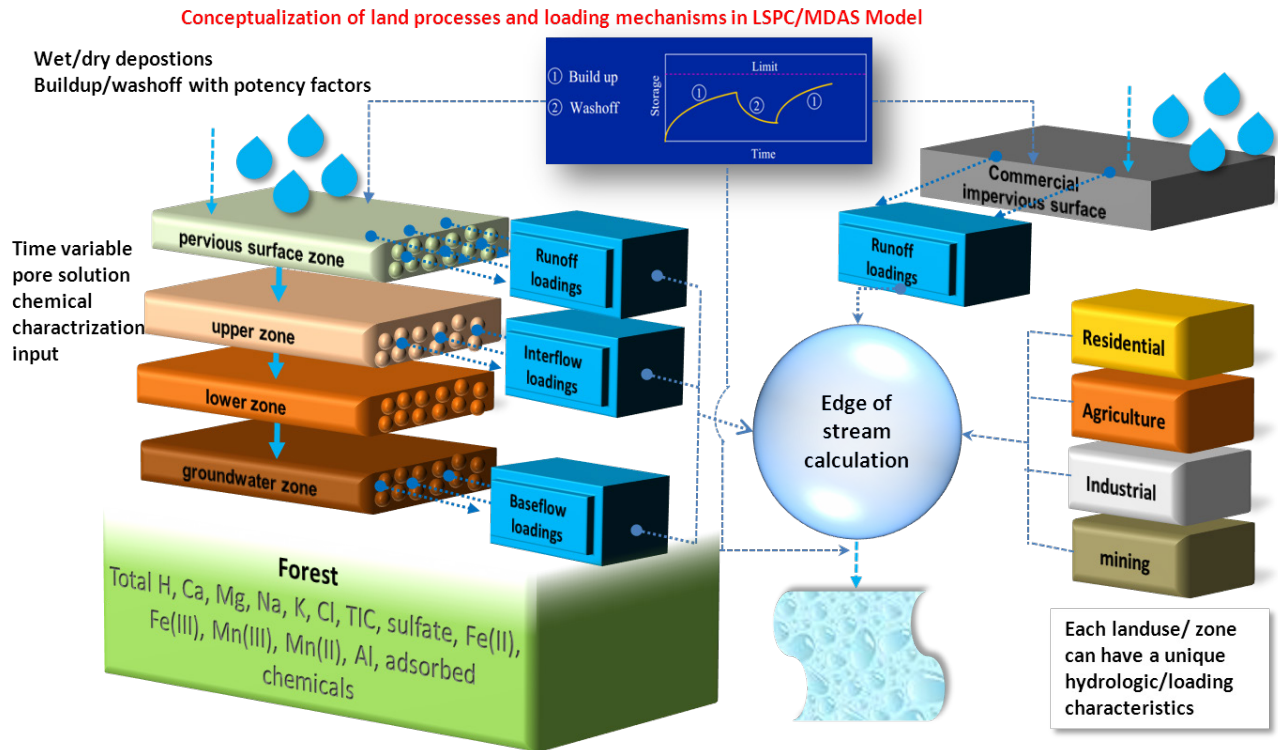


Figure 4. Land components of MDAS model.

The stream components in MDAS include the dominant processes regulating the interactions and transport of major ions, metals, adsorbing materials, and mineral phases (Figure 5). Reactions between the water column and the streambed are represented along with the reactions governing the distribution of dissolved and particulate chemicals.

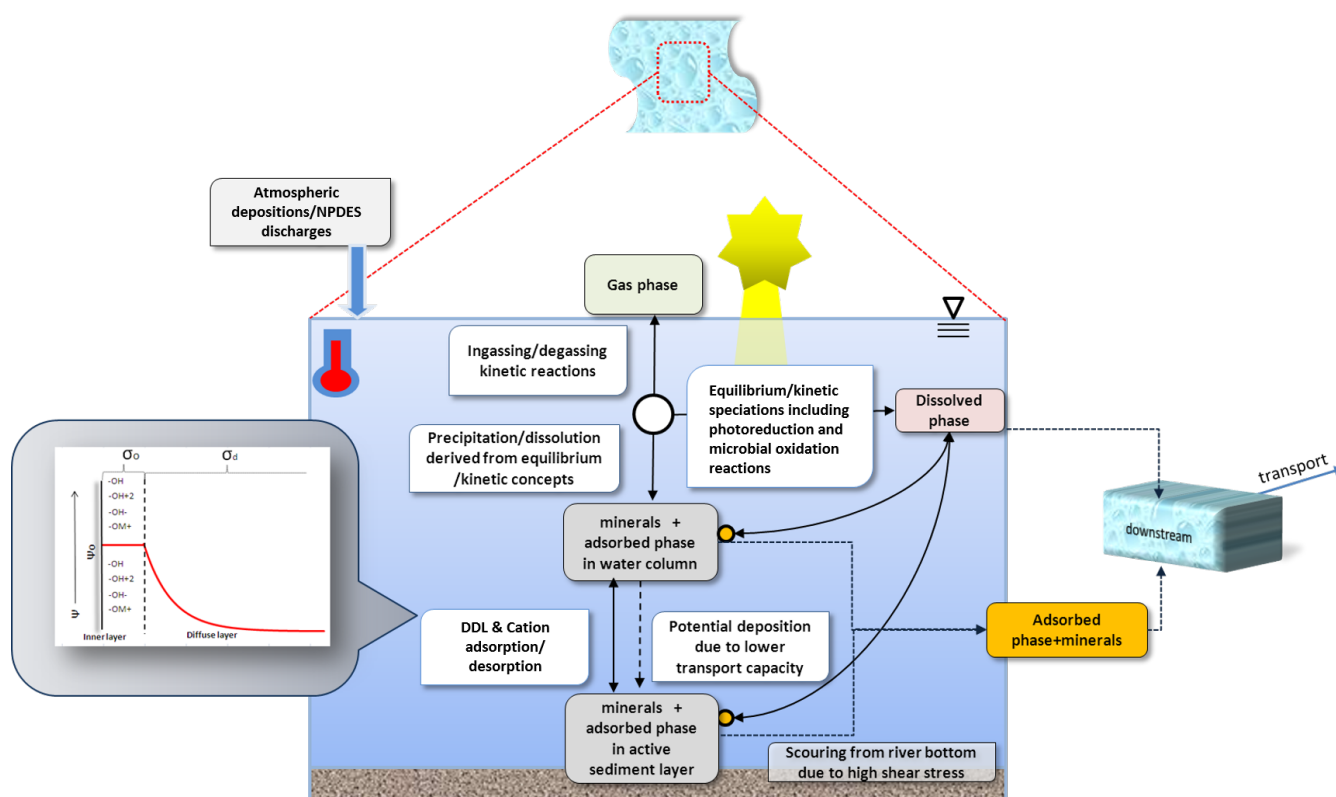


Figure 5. Stream components in MDAS.

The solution to the model equations for the reactions specified in MDAS is based on the MINTEQA2/MINEQL models with the thermodynamic database based on the MINTEQA2, Version 4.0 database. The concepts and thermodynamic data for the diffuse double layer (DDL) model for hydrous ferric oxide are based on a study conducted by Dzombak and Morel (1990). Research conducted by Tonkina, et al. (2003) and Karamalidis and Dzombak (2010) for adsorption on hydrous manganese oxide and gibbsite was reviewed, and the results were incorporated into the MDAS DDL model data. Equilibrium constants for cation and anion adsorption and desorption on clays should be selected based on the site-specific data or the literature values. Table 1 shows all significant chemical species, other than the free ions, currently included in MDAS database for a chemical system based on major ions, aluminum, iron, and manganese, and adsorption/desorption to oxides and clays. A comparison is made between the previous version and the updated version of MDAS for chemical components, complexes, species, and solids.

Table 1. Chemical components and complexes included in previous and updated versions of MDAS.

Components (previous MDAS)	Components (updated MDAS)	Aqueous Species (previous MDAS)	Aqueous Species (updated MDAS)		Adsorbed Species (updated MDAS- no adsorbed species in previous MDAS)		Solids (previous MDAS)	Solids (updated MDAS)
H ⁺	H ⁺	H ⁺	H ⁺	Fe(OH) ₂ ⁺	:FehO ⁻	KX	Iron	Iron
Ca ⁺²	Ca ⁺²	Na ⁺	Na ⁺	Fe(OH) ₃ (aq)	:Feh(OH) ₂ ⁺	CaX ₂	Aluminum	Aluminum
CO ₃ ⁻²	CO ₃ ⁻²	K ⁺	K ⁺	Fe(OH) ₄ ⁻	:FehOHCa ⁺²	MgX ₂	-	Manganese
Fe ³⁺	Fe ³⁺	Ca ⁺²	Ca ⁺²	Fe ₂ (OH) ₂ ⁺⁴	:FehOHSO ₄ ⁻²	AlX ₃	-	Calcite
Al ³⁺	Fe ²⁺	Mg ⁺²	Mg ⁺²	Fe ₃ (OH) ₄ ⁺⁵	:FehSO ₄ ⁻	FeX ₂	-	Gypsum
SO ₄ ⁻²	Mn ²⁺	Al ⁺³	Al ⁺³	FeSO ₄ ⁺	:FehOMn ⁺	MnX ₂	-	Jurbanite
H ₂ O	Mn ³⁺	Fe ⁺³	Fe ⁺²	Fe(SO ₄) ₂ ⁻	:FehO(FeII) ⁺	-	-	-
NO ₃ ⁻	Al ³⁺	SO ₄ ⁻²	Fe ⁺³	FeCl ⁺²	:FehCO ₃ ⁻	-	-	-
NH ₃	SO ₄ ⁻²	Cl ⁻	Mn ⁺²	KCl (aq)	:FehCO ₃ H	-	-	-
-	H ₂ O	CO ₃ ⁻²	Mn ⁺³	KOH (aq)	:FeO ⁻	-	-	-
-	Na ⁺	Al(OH) ⁺²	SO ₄ ⁻²	KSO ₄ ⁻	:Fe(OH) ₂ ⁺	-	-	-
-	K ⁺	Al(OH) ⁺³	Cl ⁻	MgCl ⁺	:FeOCa ⁺	-	-	-
-	Mg ⁺²	Al(OH) ₄ ⁻	CO ₃ ⁻²	MgOH ⁺	:FeOMg ⁺	-	-	-
-	Cl ⁻	AlOH ⁺²	AlOH ⁺²	MgSO ₄ (aq)	:FeOHSO ₄ ⁻²	-	-	-
-	FeOH(s)	AlSO ₄ ⁺	Al(OH) ₂ ⁺	MgCO ₃ (aq)	:FeSO ₄ ⁻	-	-	-
-	FehOH (s)	CaCO ₃ (aq)	Al(OH) ₃ (aq)	MgHCO ₃ ⁺	:FeOMn ⁺	-	-	-
-	AlOH (s)	CaHCO ₃ ⁺	Al(OH) ₄ ⁻	MnOH ⁺	:FeO(FeII) ⁺	-	-	-
-	MnOH (s)	CaOH ⁺	Al ₂ (OH) ₂ ⁺⁴	Mn(OH) ₄ ⁻²	:FeO(FeII)OH	-	-	-
-	MnhOH (s)	CaSO ₄ (aq)	Al ₃ (OH) ₄ ⁺⁵	Mn ₂ (OH) ₃ ⁺	:FeCO ₃ ⁻	-	-	-
-	X-	H ₂ CO ₃ [*] (aq)	Al ₂ (OH) ₂ CO ₃ ⁺²	Mn ₂ OH ⁺³	:FeCO ₃ H	-	-	-
-	-	HCO ₃ ⁻	AlCl ⁺²	MnSO ₄ (aq)	:AlO ⁻	-	-	-
-	-	FeOH ⁺²	AlSO ₄ ⁺	MnCl ⁺	:Al(OH) ₂ ⁺	-	-	-
-	-	Fe(OH) ₂ ⁺	Al(SO ₄) ₂ ⁻	MnCl ₂ (aq)	:AlOCa ⁺	-	-	-
-	-	Fe ₂ (OH) ₂ ⁺⁴	CaOH ⁺	MnCl ₃ ⁻	:AlOHSO ₄ ⁻²	-	-	-
-	-	Fe(OH) ₃ (aq)	CaSO ₄ (aq)	MnCO ₃ (aq)	:AlSO ₄ ⁻	-	-	-
-	-	Fe(OH) ₄ ⁻	CaCl ⁺	MnHCO ₃ ⁺	:AlOFe ⁺	-	-	-
-	-	Fe ₃ (OH) ₄ ⁺⁵	CaCO ₃ (aq)	NaCl (aq)	:AlOMn ⁺	-	-	-
-	-	FeSO ₄ ⁺	CaHCO ₃ ⁺	NaOH (aq)	:MnO ⁻	-	-	-

Table 1 (cont.)

Components (previous MDAS)	Components (updated MDAS)	Aqueous Species (previous MDAS)	Aqueous Species (updated MDAS)		Adsorbed Species (updated MDAS- no adsorbed species in previous MDAS)		Solids (previous MDAS)	Solids (updated MDAS)
-	-	-	FeOH ⁺	NaSO ₄ ⁻	:MnOCa ⁺	-	-	-
-	-	-	Fe(OH) ₂ (aq)	NaCO ₃ ⁻	:MnOMg ⁺	-	-	-
-	-	-	Fe(OH) ₃ ⁻	NaHCO ₃ (aq)	:MnOMgOH	-	-	-
-	-	-	FeSO ₄ (aq)	HSO ₄ ⁻	:MnOMn ⁺	-	-	-
-	-	-	FeCl ⁺	H ₂ CO ₃ [*] (aq)	:MnOMnOH	-	-	-
-	-	-	FeHCO ₃ ⁺	HCO ₃ ⁻	:MnhO ⁻	-	-	-
-	-	-	FeOH ⁺²	OH ⁻	NaX	-	-	-

Notes: 'h' indicates a high affinity site for chemical adsorption. Species with the same combination of components but no 'h' have a low affinity site. In reality, species with and without the 'h' are physically identical, but the designation is applied within the model to explain observed adsorption behavior.

'X' indicates a clay adsorption site.

':' indicates an adsorption surface provided by metals (Fe: hydrous ferric oxide, Al: gibbsite, Mn: hydrous manganese oxide).

The chemical loadings from the land are transported to the adjacent stream reach via the hydrologic functionalities in MDAS. The in-stream hydraulic transport is simulated in MDAS based on the complete-mix, unidirectional flow concept and kinematic wave flow routing method. MDAS's geochemical reactions within the channel are based on thermodynamics and chemical kinetics. To simulate and attain realistic stream chemical conditions, the model includes a variety of chemical reactions to support various stream conditions affected by anthropogenic or natural sources:

- Chemical speciation, including trace metals
- Acid/base chemical reactions and pH simulations
- CO₂ gas degassing/ingassing kinetics in rivers and lakes
- Redox kinetics including potential photoreduction/microbial oxidation
- Kinetic mineral precipitation/dissolution
- Adsorption/desorption based on diffuse double layer (DDL) modeling
- Cation adsorption/desorption on clay surfaces represented by cation exchange capacity
- Aging/burial of active/inactive sediment layers related to sediment deposition from the water column and scour from the stream bed

The precipitation/dissolution and the adsorption/desorption reactions both occur in the water column and streambed sediments. The heat loading into the stream from land and point sources is also considered and can be simulated. The resulting stream temperature is used for all temperature-dependent chemical reactions occurring within the stream.

The streambed consists of two virtual model layers. The first layer in the model is represented as an active sediment layer that participates in all chemical reactions. The second modeled layer is represented as a non-active sediment layer but contributes to total sediment and mineral mass. The active layer is thought to be either freshly precipitated minerals or a shallow sediment layer that reacts with chemicals/minerals in the overlaying water within the modeled computational time step. The non-active layer is assumed to be aged and has lost

chemical reactivity. Both layers are subjected to sediment aging and/or burial. The model sediments are represented by sand (as non-cohesive sediment), and silt and clay (as cohesive sediment). The cohesive sediment of the clay can be further divided into metal oxides and minerals. Minerals include solid phases, such as calcite, gypsum, jurbanite, and others, that could potentially be present in acidic/post-remedial-solution discharges from mine sources or other wastes.

Deposition to and scour from the streambed sediments are simulated on both the active and the non-active layer in the stream channel, with full simulated transport with adsorbed chemicals. The exchange between the water column and the streambed of clay, metal oxides, and other minerals is dependent on the shear stress at the benthic layer and is calculated from the reach slope and hydraulic radius.

All or some of these dissolved, particulate, and adsorbed chemicals will be transported to downstream reaches depending on the flow conditions. The transported chemicals will be subject to additional reactions and transport in downstream reaches.

While the equilibrium approach is suitable for many of the reactions in the model, additional non-equilibrium processes and reactions are represented by kinetic formulations in order to provide a greater accuracy in the stream environment. Kinetics are applied to the following:

- Degassing/ingassing of CO₂
- Lake reaeration
- Calcite dissolution and precipitation
- Metal oxides, gypsum and jurbanite dissolution and precipitation
- Metals oxidation/reduction
- Aging/burial of active sediment layer

Additional model capabilities include the previously mentioned atmospheric deposition input to the model and point source loadings addition to and subtraction from the modeled reach. The MDAS model derives total hydrogen (TH) from the edge-of-stream calculations to generate precise TH calculations and accurately represent the chemical mass balance within a stream. Point source loadings can also be added or subtracted through MDAS model configuration. Conductivity can be calculated by developing either a linear or power relationship between all dissolved chemical concentrations and the conductivity values. The coefficients and the equation should be derived from observed data to accurately model the conductivity.

The Ionic Toxicity model development will depend on the result of endpoint analysis. Based on previous studies of endpoint analysis, total dissolved solids (TDS), specific conductance (SC), and specific ionic concentrations of sulfates, bicarbonate, chloride, sodium, calcium, potassium, magnesium, can all be factors that impact the ionic stress. With the chemical speciation and thermodynamic equilibrium calculation of MDAS model, it is possible to output TDS/SC results and specific loading/concentrations of listed ions at the same time, which will keep the modeling results the most flexible for the undecided endpoint target.

Tetra Tech, as the developer of MDAS model, partnered with EPA and WVDEP, has applied this model in previous ionic toxicity pilot studies and multiple past and current TMDLs in West Virginia. The previous applications of MDAS model in West Virginia have proven that it is a solid tool to simulate both hydrological processes and geochemical reactions at watershed scale. Tetra Tech is currently developing Fecal Coliform, Total Iron, Dissolved Aluminum, and Selenium TMDLs in the Lower Guyandotte watershed with the same modeling framework. MDAS is clearly the most capable, practical, and efficient modeling tool for ionic toxicity assessment.

4.0 SUMMARY

The specific complexities in hydrological and geological conditions in West Virginia require a modeling tool with both comprehensive hydrological and geochemical process representations for the ionic toxicity TMDL development. The ongoing effort of endpoint development for West Virginia ionic toxicity requires the selected modeling tool to have capacity to simulate and output most of the ionic toxicity-related ions. Most commonly used watershed models and geochemical models either cannot simulate speciation of dissolved ions or lack the capacity to represent complicated hydrological processes such as valley fills. The MDAS model is a combination of watershed and geochemical models. It has a comprehensive representation of hydrologic processes, as well as thermodynamic-based equilibrium ion speciation simulation. The MDAS model has already been used in West Virginia watersheds for many types of TMDLs and is being used currently in Lower Guyandotte River watershed. Selecting MDAS as the model for ionic toxicity TMDL will allow leveraging of the current TMDL work to most efficiently accomplish ionic toxicity assessment. All these features and advantages of MDAS model make it a better candidate for the ionic toxicity TMDL modeling work than other models.

5.0 REFERENCES

- Allison, J.D., D. S. Brown, and K.J. Novo-Gradac. 1991. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual. EPA/600/3-91/021. U.S. Environmental Protection Agency, Washington, DC.
- Bethke, Craig, and Sharon Yeakel. *Geochemist's Workbench: Release 8.0 Reaction Modeling Guide*. RockWare Incorporated, 2009.
- Bicknell, B.R., J.C. Imhoff, J. Kittle, A.S. Donigian, and R.C. Johansen. 1996. Hydrological Simulation Program – FORTRAN: User's Manual for Release 11. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.
- Calmbach, L. "AquaChem Computer Code-Version 3.7: Aqueous geochemical analyses, plotting and modelling." *Waterloo Hydrogeologic, Waterloo, Ontario, Canada* 184 (1999).
- Chapra, S.C. 1997. *Surface Water-Quality Modeling*. WCB/McGraw-Hill, New York.
- Cormier, S M., S B. Norton, G Suter, AND D. Reed Judkins. 2001. *Stressor Identification: Technical Guidance Document*. USEPA, Washington, DC, EPA/822/B-00/025.
- Dzombak, D.A. and F.M.M. Morel. 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. John Wiley & Sons.
- Karamalidis, A.K. and D.A. Dzombak. 2010. *Surface complexation modeling: gibbsite*. John Wiley & Sons.
- New Mexico Environment Department (NMED). 2004. Total Maximum Daily Load (TMDL) for the Upper Rio Grande watershed (Part 1). <http://www.nmenv.state.nm.us/swqb/projects/RioGrande/Upper/TMDL/>
- Plummer, L. Niel, Eric C. Prestemon, and David L. Parkhurst. "An interactive code (NETPATH) for modeling net geochemical reactions along a flow path." *Water-Resources Investigations Report* 91 (1991): 4078.
- Stumm, W., and J.J. Morgan. 1996. *Aquatic Chemistry*. John Wiley, New York.
- Tipping, Edward. "WHAMC—a chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances." *Computers & Geosciences* 20.6 (1994): 973-1023.
- Tonkina, J.W., L.S. Balistrieri and J.W. Murray. 2003. *Modeling sorption of divalent metal cations on hydrous manganese oxide using the diffuse double layer model*. *Applied Geochemistry* 19: 29–53

USEPA. 2008. TMDLs for Chloride, Sulfate, TDS, and Turbidity in the Bayou Bartholomew Watershed, Arkansas. USEPA Region 6, Water Quality Protection Division, Oversight and TMDL Team, Dallas, TX.

USEPA. 2011. A Field-Based Aquatic Life Benchmark for Conductivity in Central Appalachian Streams. Office of Research and Development, National Center for Environmental Assessment, Washington, DC. EPA/600/R-10/023.

VADEQ, 2010. North Fork and South Fork Pound River Phased TMDLs for Benthic Impairments, Wise County, Virginia. Virginia Department of Environmental Quality, Water Quality Information & TMDLs, Richmond, VA.

Westall, John C. "MINEQL: A computer program for the calculation of chemical equilibrium composition of aqueous systems." *Mass. Inst. Technol.* (1976).

Wolery, Thomas J. "EQ3/6, a software package for geochemical modeling of aqueous systems: package overview and installation guide (version 7.0)." (1992).